SUPPLEMENTARY DATA:
SYNTHESIS OF GUEST MOLECULES

A large number of guest molecules are shown in Tables 1-3. With varying efficiency, these molecules were found to function as structure directing agents that ultimately end up as guests in the synthesis of zeolites SSZ-35, 36, and 39. Their syntheses are reported below (confirmation of the correct structure is determined from NMR and elemental analyses). The theoretical values are given in parentheses. The quaternary ammonium guest molecules were used in their hydroxide form after ion exchange replacement of the halide anion using BioRad AG 1-X8 ion exchange resin. All reagents are from Aldrich Chemical Co. unless otherwise stated.

Entry 1 - 29.48 grams of 3,5-dimethyl piperidine (cis/trans mixture) was dissolved in 250 mL of methanol. 37.55 grams of $KHCO_3$ were added to this solution. Methyl iodide (107.5 grams) was added dropwise while the other reagents were stirred. The reaction was stirred for several days at room temperature. The methanol solvent was stripped off, and the residual solids were then triturated with an equal volume of chloroform. Undissolved solids were filtered away, and the chloroform was stripped away. The remaining solid was then recrystallized from an excess of warm isopropanol, with just enough ethanol added to dissolve the solids. White needles were recovered after cooling the solution. 52.6 grams of 2 with a M.P. (melting point) of 273-276°C was obtained in a first crop: C = 40.28 (40.16), H = 7.27 (7.49), N = 5.19 (5.20). The iodide salt was ion exchanged to the hydroxide compound for use in zeolite synthesis. The exchange used AG 1-X8 OH resin, with the resulting solution titrated before use.

Entry 2 - The same procedure described for 1 was used with the piperidine being 3,3' dimethyl piperidine. The product had a M.P. of 275-277°C. The elemental analyses for the iodide salt were C = 40.16 (39.95), H = 7.18 (7.49), N = 5.07 (5.20).

Entry 3 - 35 grams of 3,3' dimethyl piperidine were placed in 300 mL of methanol. 70.2 grams of ethyl iodide, which had been passed through a short column of aluminum oxide, was added into solution; and the reaction was heated to reflux using a heating mantle and while stirring. The reaction was followed by thin-layer chromatography and cooled after a few days. Diethyl ether was added to force the solids out of solution. The solids were then dissolved in 200 mL of water and the pH subsequently adjusted to 12 using 50% NaOH. The product was collected via three 200-mL extractions with methylene chloride. The extracts were dried over Na_2SO_4, and the latter was then filtered off and the solvent stripped. 37.69 grams of the N-ethyl piperidine derivative was recovered as an oil. This tertiary amine was now suspended in 200 mL of methanol, and the same reaction was carried out as in Entry 1 (13.36 grams of $KHCO_3$ and 76.5 grams of methyl iodide). The product was recovered from recrystallization from hot isopropanol and acetone, and has a M.P. of 272-273°C. It analyzed for C = 42.34 (42.41), H = 7.65 (7.83), and N = 4.74 (4.95).

Entry 4 - 47.17 grams of 2-ethyl piperidine was reacted with 93.58 grams of ethyl iodide in 400 mL methanol in a manner like Entry 3 above. After 2 days the reaction was stopped; and with similar work-up, 37.2 grams of oil was collected. 18.6 grams of this oil was reacted with another charge of ethyl iodide (41 grams) and 6.59 grams of potassium bicarbonate in 130 mL methanol at reflux. After the work-up as in 3, and recrystallization from hot acetone/isopropanol, 20.27 grams of crystals were collected with M.P. = 252-254°C. C = 44.49 (44.45), H = 7.60 (8.14), N = 4.70 (4.71).

Entry 5 - The product was prepared as in 1, starting with 2-ethyl piperidine. M.P. = 278-279°C; C = 40.55 (40.16), H = 7.53 (7.49), N = 5.13 (5.20).

Entry 6 - Starting with 2-methyl piperidine, the same reaction as in Entry 4 was carried out to make the mono N-ethyl derivative. The product oil was then reacted with excess

methyl iodide (dropwise) in methanol. After forcing the product out with ether, the solids were recovered and recrystallized from acetone/methanol. A third crop, the largest fraction collected, had M.P. = 301-304°C. Analyzed as C = 39.93 (40.16), H = 7.54 (7.49), N = 4.81 (5.20).

Entry 7 - 22.87 grams of 2,6 dimethyl piperidine was placed in a reaction flask with 50 mL methanol and 30 grams potassium bicarbonate as base. With dropwise addition, 61.94 grams of 1,4 diodobutane were added. The reaction was stirred at room temperature for 4 days. Next the methanol was stripped off. The residual solids were treated with 100-200 mL chloroform and the undissolved solids were removed. The remaining solution was treated with diethyl ether until solids precipitated. The solids were dissolved in 200 cc water and the pH was adjusted to 12. Three, 100-mL extractions were carried out with methylene chloride. The extracts were dried with sodium sulfate. The dried solution was then stripped off and the solids were recrystallized from hot acetone/methanol. The resulting crystals have M.P. = 280-282°C and C = 44.77 (44.76), H = 7.53 (7.51), N = 4.45 (4.75).

Entry 8 - The same type of reaction as in 7 was carried out except 3,3' dimethyl piperidine was reacted with 1,4 dibromopentane. The work-up was in the same manner as 7, except skipping the basification with water and proceeding directly to recrystallization (acetone/methanol); after recovery in chloroform, yielded a product with a M.P. = 256-258°C. It analyzed as C = 54.88 (54.96), H = 9.17 (9.22), N = 5.13 (5.34).

Entry 9 - The synthesis of N-methyl camphidinium is described in four steps in the patent to Nakagawa [1].

Entry 10 - Exhaustive methylation of bornylamine was carried out as in Entry 9.

Entry 11 - The skeleton for this polycyclic molecule was constructed from the use of a Mannich reaction. A 5-liter flask was set up with condenser and nitrogen sweep capability. 140 grams of glutaraldehyde and 630 mL of water were placed in the flask. 70.66 grams of

methylamine hydrochloride in 700 mL water was added next. 116.6 grams of acetone dicarboxylic acid in 1162 grams of water was added in; and also, a solution 123 grams of sodium phosphate, dibasic, and 10.22 grams of NaOH (s) in 280 mL water were placed in the flask. The reaction was stirred at room temperature, and a bubbler was used to monitor gas sweep and evolution. Next we added 46 mL of concentrate HCl and refluxed for 1 hour to complete the decarboxylation. Then we added 105 grams of NaOH (s) in 140 mL of water followed by 8 extractions (250 mL each) with methylene chloride. Dry the extracts over sodium sulfate and strip down. 103 grams was collected. Next, the carbonyl functionality was reduced via a Wolff-Kischner reduction. 44 grams of the oil were added into a 2-liter flask also containing 1351 mL of triethylene glycol, 148 grams of KOH (s), and 36.75 grams of hydrazine, which were added last and slowly to contain the exotherm. Slowly bring the reaction to reflux and maintain for 8 hours. Upon cooling, replace the condenser with a distillation head. Next, we added boiling chips to the flask and began to raise the temperature. We collected distillate until the head temperature was 215°C. We extracted the distillate with chloroform (2 x 150 mL). Then we added 150 mL of water to the extracts and lowered the pH below 2. We repeated a second low pH treatment of the chloroform phase. Next we added NaOH to bring pH above 12 and back-extracted with ether (4 x 200 mL). These were dried over sodium sulfate and stripped. This produced the free, tertiary amine. 7.0 grams of the amine was reacted with ethyl iodide in chloroform. The resulting product was recrystallized from hot methanol/ether to give a M.P. = 316-319°C. The product analyzed for C = 44.80 (44.75), H = 7.59 (7.51), and N = 9.53 (9.44).

Entry 12 - Starting with tropinone, the same Wolff-Kischner reduction and subsequent alkylation was carried out as in Entry 11: C = 42.53, H = 7.03, N = 4.97.

Entry 13 - Bicyclo [3.3.1] nonane–9-one was converted to the lactam as follows: 8.67 grams of the ketone was placed in 61 mL formic acid (96%). With an addition funnel,

10.86 grams of hydroxylamine-o-sulphonic acid in 32 mL formic acid were added dropwise. The mixture was refluxed for 24 hours. Next we poured the reaction onto 500 grams of ice and then adjusted the pH to above 12 with 50% NaOH. We extracted with methylene chloride (3 x 100 mL), dried with sodium sulfate, and then stripped down. Using a column of 120 grams of silica gel (230-400 mesh) slurried into chloroform, the oil was loaded in a minimum of chloroform; and then the column was eluted with 98/2 chloroform/methanol. Following the fractionation by TLC, 4.85 grams of the lactam were recovered after stripping down the relevant fractions. The lactam was reduced to the amine using lithium aluminum hydride (LAH, caution in using). A three-neck, 200-mL round bottom flask with condenser, gas bubbler, and addition funnel was set up. 1.86 grams of LAH was carefully added to 46 mL anhydrous ether in the flask. 4.75 grams of lactam in 23 mL methylene chloride was added slowly from the addition funnel. A dry ice/acetone bath was used to control temperature. As the reaction was stirred and allowed to come to room temperature, it was monitored by TLC for the loss of the lactam. By the next day the reaction looked complete. Carefully we added 1.9 grams of water, generating considerable gas evolution. Next, 1.9 grams of 15% NaOH was added; and then an additional 5.6 mL of water was added last. After stirring for a while, the solids were filtered off and washed with additional methylene chloride. The combined organic solutions were treated first with acidic solution, and then the high pH modification and ether extraction was carried out as in Entry 11 to liberate the amine. 3.80 grams of the amine were alkylated with methyl iodide as in Entry 1. Recrystallization from hot isopropanol/methanol yielded slightly purple flakes. The M.P. was 300-302°C and C = 44.90 (44.75), H = 7.57 (7.51) and N = 9.61 (9.43).

Entry 14 - This guest molecule was constructed from a single ring construction step via Michael Addition between a lithium-stabilized dienolate and an activated olefin. Then a number of side-chain modification steps were carried out, finally leading to a ketone. The

ketone is transformed to lactam, amine, and quaternary ammonium product in the same sequence of steps as given for Entry 13. A three-neck, 5-liter flask was set up with additional funnel with equalization arm. A septum was placed over the funnel. Nitrogen was passed through the system. First an in-situ reagent was developed by placing 104.55 grams of diisopropylamine in 1859 mL of tetrahydrofuran (THF) and then slowly adding 401.7 mL of n-butyl lithium (2.5 M in hexane) while keeping the temperature near –70°C. The n butyl lithium was charged to the addition funnel by use of a cannula. The addition into THF took about 1.25 hours. Then stir for another hour. 104.53 grams of 3-methyl-2- cyclohexene-1 one in 1117 mL THF was added dropwise over a 0.75-hour period. Lastly, we added 161.73 grams of methyl acrylate over a period of 0.25 hour. Gradually we allowed the reaction to warm to room temp and followed the progress by TLC. The reaction appeared to go overnight. The work-up was begun by adding 1N HCl until the solution became acidic. Next, transfer to a separatory funnel and recovered the aqueous phase to subsequently treat with methylene chloride (2 x 250 mL). We dried the combined organic phase over sodium sulfate and then stripped the solvent. The residue was taken up in ether to free it from a little gummy material. The ether is removed and the oil was distilled; a Vigreaux column (30 cm) was set up and run at 2-4 mm Hg. The bulk of the product came over between 123-137°C. A number of earlier studies have indicated that the stereochemistry for this first ketoester product have both carbonyls (C_2 and C_5) syn to each other [2a-c]. This product was next reduced using the same LAH reduction procedure described for Entry 13. The reduction produced a diol, 1-methyl, 2-methanol, 7 hydroxy bicyclo [2.2.2] octane. The side methanol group was tosylated by reaction of tosyl chloride (96.92 grams) with the diol (85.68 grams) in anhydrous pyridine (500 mL). The tosyl chloride was added to the other two components, under nitrogen, via addition using a powder addition funnel while cooling the reaction to –5°C. The addition was carried out over 0.75 hour. It was warmed to room

temperature and run overnight. Next, we added 500 mL methylene chloride, transferred to a separatory funnel, and washed with water (2 x 250 mL). It was dried over sodium sulfate, filtered, and stripped to yield 150 grams of oil. The product was purified by column chromatography. A kilogram of silica gel (230-400 mesh) was slurried in hexane, and the oil was loaded on top in 50 mL methylene chloride. The elution was carried out using 25/75 ethyl acetate (ETOAC); hexane and fractions were monitored by TLC. 83 grams of product was collected. The tosylate was then reduced using LAH (as above) to yield 1,2-dimethyl, 7 hydroxy bicyclo [2.2.2] octane. Next, the alcohol was reoxidized to the ketone. 37.84 grams of the alcohol were reacted in a three-neck, 2-liter flask as follows: 34.60 grams of oxalyl chloride and 604 mL of methylene chloride were loaded in and blanketed under nitrogen. With an addition funnel with side arm, 46 grams of anhydrous dimethylsulfoxide (DMSO) in 122.7 mL of methylene chloride were added. The bath was cooled to –60°C using a dry ice/acetone bath, and the addition took 0.5 hours. The alcohol, in 53.4 mL methylene chloride, was added at this temperature over 0.5 hour. We stirred another 0.5 hour. Next, we placed 126.65 grams of triethylamine in the addition funnel, and began addition and continued over 0.25 hour. All of the additions produced exothermic responses, so we continued to cool. Slowly the reaction was warmed to room temperature and continued to run overnight. The work-up began with the addition of 500 mL water. The separated aqueous phase was then extracted with methylene chloride (2 x 250 mL). The combined organic phases were then dried over magnesium sulfate and then stripped. The oil was triturated with ether to separate a small amount of insoluble material. Stripping off ether yielded 37 grams. The product ketone was then carried through the same oxime-to-lactam-to-amine steps as in Entry 13. This yielded a mixture of two amine isomers (nitrogen at ring position 2 or 3). The mixture was alkylated with methyl iodide, as

described in Entry 1. Recrystallization from hot acetone/methanol gives the 2-position isomer selectively (M.P. = 278-281°C).

Entry 15 - The synthesis of the eventual target molecule began with the reaction of 98 grams of (1R)-(-)-fenchone (as the ketone) with 112 grams of hydroxlamine-o-sulfonic acid in formic acid (970 mL total) as described above. Two isomeric lactams may form. The lactams were collected via chromatography, as described above. Next, reduction was carried out using LAH, as described above. Alkylation, as in Entry 1, was carried out. Recrystallization from hot acetone/methanol yielded flakes, M.P. = 274-275°C.

Entry 16 - The same procedures were carried out as in Entry 15, starting with 64.53 grams of trans-1-decalone. The last step was alkylation with ethyl iodide, as in Entry 4. The product from hot acetone/methanol had M.P. = 214-217°C.

Entry 17 - The same lengthy reaction sequence as in Entry 14 was begun with 90 grams of 3-methyl-2-cyclohexen-1-one, but the addition component this time was 163.56 grams of methyl crotonate (replacing the previous methyl acrylate). The same sequence of steps was carried out: LAH reduction to diol, formation of tosylate, re-reduction, oxidation to the mono ketone, formation of the oxime, rearrangement of the lactam, reduction to the amine, methyl iodide alkylation, as in Entry 1. Recrystallization from hot acetone/isopropanol yielded M.P = 250-255°C.

Entry 18 - The same reaction as in Entry 14 was carried out but using isophorone (119 grams) as the entry ketone. The final alkylation step, as in Entry 1, yielded solids with M.P. = 226-228. NMR shows a mixture of isomers for nitrogen at 2 or 3 position.

Entry 19 - The entry ketone, in this instance, was first prepared by hydrogenating 20 grams of the unsaturated keto compound, verbenone, using 2 grams of Pd on activated carbon in 200 mL absolute ethanol. The reduction was carried out in a Parr hydrogenator at 60 psi

hydrogen. The reaction mixture was filtered through a short column of celite/silica gel, rinsing with ethanol. A different procedure was used this time for a two-step formation of the oxime and then lactam. 72.9 grams of the ketone was combined with 40.34 grams of hydroxylamine hydrochloride, 78.57 grams of sodium acetate (trihydrate), 435 mL ethanol, and 218 mL water. This mixture was then refluxed for about 2 hours. The cooled mixture was worked up by pouring into a brine solution and extracting with chloroform (3 x 250 mL), drying over sodium sulfate, and then stripping. The lactam was formed next by reacting 88 grams of the oxime with tosyl chloride (153 grams), potassium carbonate (185 grams) in 768 mL dimethoxy ethane, and 666 mL water. This mixture was refluxed for 6 hours (80°C). Next, we removed the dimethoxyethane in a rotoevaporator. The aqueous phase was extracted with chloroform (3 x 250 mL), and the latter was washed once with 300 mL brine and then dried over sodium sulfate. 76 grams of oil was recovered. Purification was carried out on silica gel (2 kg) slurried in hexane and used as described above, and gave 58 grams of isolated product. The same steps were then carried out to reduce (LAH) the lactam and alkylate (Entry 1) to the dimethyl ammonium derivative. Recrystallization from hot acetone gave a product with M.P. = 215-220°C.

Entry 20 - The same procedure as described above for Entry 19 was used to transform 40 grams of (1R)-(+)- nopinone to the lactam. Subsequently, the same LAH reduction and methyl iodide alkylation steps were carried out. From hot acetone/isopropanol, a product was recovered with M.P = 241-245°C.

Entry 21 - This compound was prepared from 3 aza bicyclo [3.2.2] nonane reacting with methyl iodide, as in Entry 1.

Entry 22 - Using the same amine as in Entry 21 and the procedure for Entry 3, the mixed methyl/ethyl derivative was made. The product was recrystallized from hot

acetone/methanol and a slight bit of ether. M.P = 256-258°C and C = 43.50 (44.75), H = 7.69 (7.51), N = 4.61 (4.74) C/N = 9.44 (9.44).

Entry 23 - Alkylation as in Entry 1 was carried out for 1,3,3, trimethyl-6-aza bicyclo [3.2.1] octane

Entry 24-26 - The preparation of these compounds has already been described in part [3-5]. The skeleton of these 3,7 diazabicyclo [3.3.1] nonanes is formed by reacting N-substituted 4-piperidones with a mixture of methylamine hydrochloride, glacial acetic acid, and paraformaldehyde. The resulting 9-keto group is eliminated by Wolff-Kischner reduction, as has been described above for Entry 11. Subsequent alkyl halide addition to the secondary or tertiary amine gives the desired product.

Entry 27 - Starting with bicyclo [3.2.1] octan-2-one, the same oxime and lactam transformations were carried out as in Entry 19. LAH reduction lead to the amine, and the dimethyl quaternary derivative was formed as in Entry 1. Recrystallizing from hot acetone/methanol gave a solid with a decomposition temperature near 290°C. By NMR, the product was a 3/1 mixture of the two isomers with 2N position over 3N position.

Entry 28 - The reaction was started with the available lactam, 2-aza-tricyclo [4.3.3.1] undeca-3-one. LAH reduction followed by alkylation, as in Entry 1, gave the product.

Entry 29 - The Diels-Alder reaction was carried out between freshly cracked cyclopentadiene and cyclopentene 1,2-anhydride using previous methods [6]. The anhydride was converted to the imide by refluxing in 40% methylamine (water) with a catalytic amount of N-dimethyl-4-pyridine (DMAP). The reaction is best carried out using a Parr Teflon-lined pressure vessel where the reaction can be carried out in a closed container at 80-90°C (CAUTION: Calculate the potential pressure and work with large void space.) The resulting imide was reduced with LAH, and the alkylation was carried out as in Entry 1.

Entry 30 - Using a previously published procedure, the enamine was formed for 3-chloro cyclohexene reacting with pyrrolidine [7]. This compound (27 grams) was reacted with freshly cracked cyclopentadiene in a Diels-Alder reaction. In a dry reaction flask and under nitrogen sweep, 520 mL of methylene chloride was used as solvent for 34 grams of silver tetrafluoroborate. This was cooled to –78°C (dry ice/isopropanol), and 25 grams of the diene was stirred in. Lastly, the chloroenamine, in 70 mL of methylene chloride, was added dropwise and kept at this temperature for 4 hours. It was slowly brought to room temperature and continued for 12 hours. The reaction was filtered through a pad of celite and concentrated. Next, this intermediate product was taken up in 200 mL water, 100 mL methanol, and 23 grams of NaOH to drive the formation of the ketone. We refluxed for 7 hours and then stripped off the methanol. The basic aqueous solution was extracted with 200 mL ether. Drying over magnesium sulfate and stripping gave a single compound by NMR (62 grams of solid). This polycyclic ketone was converted to the oxime. The reaction was carried by using 1 equivalent of the ketone, 5.5 for hydroxylamine hydrochloride, 40 mL pyridine in 160 mL methanol. Refluxing was carried out for 1.5 days. The double bond in the other ring was removed via hydrogenation in 100 mL absolute ethanol and 0.25 gram of Pd on carbon for 4.4 grams of olefinic, polycyclc oxime. Hydrogen was used in a Parr hydrogenator at 42 psi. The work-up was as in Entry 19. The lactam was formed via use of tosyl chloride in pyridine. For 1 gram of oxime, 3.5 grams of tosyl chloride was mixed in 75 mL pyridine. The mix was stirred at room temperature overnight and then refluxed at 80°C for 2 hours. The reaction was concentrated under reduced pressure and then passed through a silica gel plug using methylene chloride to collect material. Finally LAH reduction was carried out, followed by methyl iodide alkylation.

Entry 31 - The 3 position of norcamphor was alkylated using 1-chloro-4-iodobutane, reacting 72 grams of the ketone with 178.5 grams of the dihalide, facilitated by the

in-situ reagent generated from diisopropylamine (78 grams) and 295 mL of 2.5 M n-butyl lithium in hexane. 900 mL of anhydrous THF was used as solvent. The sequence of addition steps was as in Entry 14. The reaction was slowly allowed to come to room temperature after all reagents had been added and stirred. It was then stirred at room temperature for 4 days. The work-up was carried out by partitioning the reaction products between 500 mL of 2N sulfuric acid and 3 liters of ether. The separation must be vigorously shaken. The ether phase was next washed with 500 mL brine, dried over sodium sulfate, and concentrated, yielding 161 grams of a brown oil. A column was prepared using 2 kg of silica gel slurried in hexane as described before. The elution was carried out using a sequence of ETOAC/hexane of 5/95 = 2 gallons, 7.5/92.5 = 1 gallon, and then 10/90 = 1 gallon. By following the fractions with TLC, 122.5 grams of an orange oil was recovered. This was the product with a 4-chlorobutane ring substituent. The butyl termini was next transformed to the azide by treating 122.5 grams of the previous step product with 200 grams of sodium azide (Caution) in a liter of DMF, heating at 80°C for 4 hours. The reaction was poured into 5 liters of ether, extracted using water and then brine, dried, and then stripped. The azide product undergoes a ring closure by stirring (under nitrogen) 119 grams of it in 2300 mL of a 1M solution of titanium tetrachloride in methylene chloride. It was stirred for 4 days. Transferring the reaction mixture to a separatory funnel large enough for addition of 4 liters of ETOAC, we washed the organic phases with a liter of saturated sodium carbonate solution and then with 500 mL of saturated sodium chloride solution. Drying over sodium sulfate and concentrating yielded 29 grams of oil. Back-extracting the aqueous phases with chloroform (3 x 500 mL) yielded 85 grams of oil. Both isolated materials are the same by TLC. Next we purified further using column chromatography. 1.5 kg of silica gel (230-400 mesh) slurried in chloroform has the compound loaded on, and elution was begun using 2/98 methanol/chloroform. Collection of relevant fractions yielded 88 grams of the lactam. The

lactam was next reduced in methylene chloride/ether using LAH, as described for Entry 14. 16.5 grams of the recovered tertiary, bridgehead amine was dissolved in methanol and alkylated with an excess of methyl iodide. Work-up and eventual recrystallization from hot acetone/isopropanol yielded crystals with M.P. = 260-262°C.

Entry 32 - This product was prepared as in Entry 30 except the starting ketone was 2-chloro cyclopentanone and the second Diels-Alder component used was furan.

Entries 33 & 34 - These two isomeric products were separately recovered from a reaction like Entry 30, except the same starting ketone as in Entry 32 was used.

Entry 35 - The same lactam was used as in Entry 28. Once the secondary amine was obtained, the product was generated in two steps, as in Entry 3. Recrystallization of the final product from hot isopropanol/methanol gave a product with M.P. = 284-287°C. The analyses were C = 48.75 (48.61), H = 7.62 (7.53), N = 4.34 (4.36).

Entry 36 - 1-Adamantanol was oxidized with iodine in the presence of lead (IV) acetate. In a 5-liter flask equiped with mechanical stirrer, nitrogen sweep, reflux condenser, and a heating mantle controlled by a Thermo-watch, 2400 mL of anhydrous benzene was used as solvent for 40 grams of adamantanol, 233 grams of the lead acetate, and 149.6 grams of iodine. The reaction was brought to 70-75°C after reagent addition. The very thick, jamlike solution becomes difficult to stir during the heat-up. About an hour was used to reach temperature, and then the reaction was held there for 2 hours. Next, cool to room temperature, filter off solids, and wash solids with ether (3 x 400 mL). The organic collections were combined and shaken against 2 liters of sodium bisulfite until the dark red color has disappeared. Continue a cycle of letting the separation stand and reshaking if the color comes back after 15 minutes of standing. The organic layer was eventually washed with 1 liter of water and then 1.5 liter of saturated sodium bicarbonate. (Caution: Much gas evolution occurs.) Dry over magnesium sulfate and

then remove the solvent below 30°C because of thermal instability of the product. Nearly 100 grams (still contains a little benzene) of this iodomethylene, fragmented adamantanone, was stirred in 600 mL methanol and with 28 grams of KOH (s) was brought to reflux for 3 hours. The reaction mixture was poured onto 1.2 kg ice. We extracted with ether (5 x 400 mL), dried over magnesium sulfate, and recovered 36 grams of yellow solid. This product is the tricyclo [5.2.1.0] deca-3-one. 8.54 grams of this ketone were given the one-step oxime/lactam formation, as in Entry 13 above. Following LAH reduction, the secondary amine (potential mix of two isomers) was alkylated using methyl iodide, as in Entry 1. The NMR of the product indicated that it is mainly the isomer shown as Entry 36. M.P. = 290-292°C after recrystallization of hot isopropanol. C = 47.46 (46.91), H = 7.00 (7.22), N = 4.54 (4.56), C/N = 10.45 (10.29).

Entry 37 - Starting with the lactam in Entry 28, the amine was formed via LAH reduction. The alkylation using ethyl iodide was carried out in a single step. 10 grams of the amine was stirred in 66 mL methanol with 9.93 grams of potassium bicarbonate. 31 grams of ethyl iodide were added and the reaction was brought to reflux. After heating for a day and work-up as in Entry 1, recrystallization from isopropanol/methanol yielded yellow flakes with M.P. = 270-272°C. C = 49.92 (50.15) H = 7.83 (7.82), N = 4.12 (4.18).

Supplemental References

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:kad/brp/990915-Zones

Supplementary Data Table 1

Atomic Positions (Fractional Coordinates) and Isotropic Temperature Factors for SSZ-39 (*C 2/c*) a = 13.6297 Å, b = 12.6748 Å, c = 18.4730 Å, and ß = 89.93°

Atom Type	x	y	z	U(iso)Å^{-2}
Si	0.11159	0.03790	0.16534	0.01471
Si	0.11328	-0.22654	0.93775	0.02062
Si	-0.22714	-0.09529	0.05226	0.05319
Si	0.22932	-0.09570	0.05101	-0.00594
Si	-0.11313	-0.22908	0.93902	0.03501
Si	-0.11105	0.03380	0.16475	0.03439
O	-0.18007	-0.05243	0.12515	0.00773
O	-0.14485	-0.16607	0.01273	0.02557
O	0.00040	-0.25831	0.94681	0.02381
O	0.14462	-0.16428	0.01175	0.02403
O	0.18183	-0.04770	0.12304	0.01765
O	0.00011	-0.00107	0.15120	0.02052
O	-0.13014	0.14934	0.12994	0.02213
O	-0.32056	-0.16798	0.07195	0.03172
O	0.13930	0.03967	0.25047	0.02809
O	0.17957	-0.33080	0.92823	0.03063
O	-0.12989	-0.15161	0.87053	0.02080
O	-0.26008	0.00046	1.00150	0.01006